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A PROCESS FOR DECREASING ENVIRONMENTAL POLLUTANTS IN AN OIL OR A FAT, A VOLATILE FAT OR OIL ENVIRONMENTAL POLLUTANTS DECREASING WORKING FLUID, A HEALTH SUPPLEMENT, AND AN ANIMAL FEED PRODUCT

TECHNICAL FIELD OF THE INVENTION

This invention relates to a process for decreasing the amount of environmental pollutants in a mixture comprising a volatile working fluid and a fat or an oil, being edible or for use in cosmetics, containing the environmental pollutants, which process comprises stripping from the mixture the volatile working fluid and the environmental pollutants. The present invention also relates to a second process with the same purpose as presented above, which process comprises thin-film evaporation. In addition, the present invention relates to a volatile fat or oil environmental pollutants decreasing working fluid, a health supplement, a pharmaceutical and an animal feed product prepared according to at least one of the processes mentioned above.

BACKGROUND OF THE INVENTION

DDT (2,2 bis-(p-chlorophenyl)-1,1,1-trichloroethane) and its degradation products are today found almost everywhere in the global environment. Numerous studies also report on the accumulation of often relatively high concentrations of pesticides like PCB, DDT and its metabolites, toxaphenes, dioxins and brominated flame retardants in the deposit of e.g. marine organisms. The hazard of these compounds for both humans and animals have caused a growing concern about the content of toxic substances in food and food stuff. Consumption of dioxins above safe levels over a lifetime may result in an increased risk of cancer.

Food products that have no or reduced amounts of pollutants are gaining popularity as well as an increasing share of the market. Consequently, removal or reduction of pollutants in food products have the potential to substantially increase marketability and value.

The commercially important polyunsaturated fatty acids in marine oils, such as fish oil, are preferably EPA (eicosapentaenoic acid, C20:5n-3) DHA (docosahexaenoic acid, C22:6n-3). The full nomenclature of these acids according to the IUPAC system is: EPA all-cis-5,8,11,14,17-eicosapentaenoic acid, DHA all-cis-4,7,10,13,16,19-docosahexaenoic acid. For many purposes it is necessary that the marine oils should be refined in order to increase the content of EPA and/or DHA to suitable levels, or to reduce the concentrations of, or even eliminate, certain other substances which occur naturally in the raw oil.

The fatty acids EPA and DHA are also proving increasingly valuable in the pharmaceutical and food supplement industries in particular. It is also very important for fish oils and other temperature sensitive oils (e.g. oils that contain long chain polyunsaturated fatty acids) to keep the temperature in some of the processes as low as possible.

The demand for marine oils of high quality is increasing. This issue forces the fish oil industry to consider use of alternative refining techniques for fish oils with inferior quality, i.e. oils with high amounts of free fatty acids that make the oils less useful for nutritional purposes and make traditional alkaline refining more complicated and costly. If environmental pollutants can be successfully removed from such fish oils they are appropriate to be used in the animal feed industry, e.g. in animal feed products.

From the literature it is known that molecular distillation, or short path distillation as the technique alternatively may be named, can be used to remove pesti-

cides from fish oil (K. Julshamn, L. Karlsen and O.R. Braekkan, Removal of DDT and its metabolites from fish oils by molecular distillation, Fiskeridirektoratets skrifter; Serie teknologiske undersøkelser, Vol. 5 No.15 (1973)). However, the effect of this method is limited to the pesticide DDT. A practical upper limit was 65% removal together with a loss of about 25% of vitamin A.

Anthony P. Bimbo: Guidelines for characterization of food-grade fish oil. INFORM 9(5), 473-483 (1998), reported that vacuum stripping or thin-film distillation can be used to remove chlorinated hydrocarbons and free fatty acids from fats or oils. A disadvantage by using vacuum stripping to refine oils is that sufficient results only can be achieved then the vacuum stripping process is carried out at a high temperature. Further, the high temperature gives rise to undesirable side reactions.

Jiri Cmolik og Jan Pokorny: Physical refining of edible oils, Eur. J. Lipid Sci. Technol. 102(7), 472-486 (2000) describes physical refining of edible oils and the use of molecular distillation for removal of undesirable substances in crude oils, preferably crude vegetable oils, respectively the use of steam stripping in order to remove free fatty acids from an oil composition. Physical refining is used to refine oils of good quality, i.e. oils with small amounts of free fatty acids. However, physical refining is more complicated and costly for oils with inferior quality.

In WO 9524459 a process for treating an oil composition containing saturated and unsaturated fatty acids in the form of triglycerides, in order to obtain a refined product with higher concentrations of the polyunsaturated fatty acids, is presented. This process is intended to be used also for removal of environmental pollutants from an oil composition, wherein the process comprises the steps of; subjecting the oil composition to a transesterification reaction and thereafter subjecting the product ob-

tained in the first step to one or more molecular distillations.

In EP0632267 A1 a method of measuring the content of polycyclic aromatic hydrocarbons(PAH) remaining in lanolin is presented. The European patent document also describes a method of removing PAH remaining in wool grease or lanolin by a vacuum distillation of the grease or lanolin under specified conditions either directly or after having been treated with a borate and, if necessary, obtaining various lanolin derivatives from the treated wool grease or lanolin.

Another interesting observation is that the removal of environmental pollutants from fats or oils is not a trivial matter. Several different techniques, some of which mentioned above, to accomplish this task have been developed, but none of them is sufficiently effective and gentle to the fat or oil. In addition, it is nowadays a problem for e.g. the marine oil industry that the amounts of pollutants in e.g. fish oil has become increased.

SUMMARY OF THE INVENTION

One object of the present invention is to offer an effective process for decreasing the amount of environmental pollutants in a fat or an oil, being edible or for use in cosmetics.

According to a first aspect of the invention, this and other objects are achieved with a process for decreasing the amount of environmental pollutants in a mixture comprising a volatile working fluid and a fat or an oil, being edible or for use in cosmetics, containing the environmental pollutants, which process comprises stripping from the mixture the volatile working fluid and the environmental pollutants, wherein the volatile working fluid comprises at least one of a fatty acid ester, a fatty acid amide, a free fatty acid and a hydrocarbon.

The use of a volatile working fluid in a stripping process for decreasing the amount of environmental pol-

lutants in a fat or an oil, being edible or for use in cosmetics, has a number of advantages.

An advantage of using a volatile working fluid in a stripping process is that the environmental pollutants can more easily be stripped off together with the volatile working fluid. This is possible as long as the volatile working fluid is equally or less volatile than the less volatile pollutant that shall be removed.

In addition, the use of a volatile working fluid comprising at least one of a fatty acid ester, a fatty acid amide, a free fatty acid and a hydrocarbon in a stripping process results in that use of the inventive process decreases the amount of dioxins in a fish oil with more than 95%. Another advantage of adding a volatile working fluid to an oil prior to a stripping process is that removing of free fatty acids is facilitated, which will result in a higher quality of the oil product.

In addition, the volatile working fluid according to the invention allows environmental pollutants to be stripped off by e.g. molecular distillation even from oils of lower quality.

In a preferred embodiment of the present invention the volatile working fluid is an organic solvent or solvent mixture with a volatility comparable to the environmental pollutants. Namely, the volatile working fluid of the present invention is at least one of a fatty acid ester, a fatty acid amide, a free fatty acid and a hydrocarbon, also including any combinations thereof. Preferably, the volatile working fluid is at least one of esters composed of C10-C22 fatty acids and C1-C4 alcohols, amides composed of C10-C22 fatty acids and C1-C4 amines, C10-C22 free fatty acids, and hydrocarbons with a total number of carbon atoms from 10 to 40. Most preferably, the volatile working fluid is a mixture of marine oils, e.g. fish body oil and/or fish liver oil, and/or ethyl esters of marine fatty acids.

In another preferred embodiment of the process the volatile working fluid is constituted by free fatty acids comprised in the fat or oil, being edible or for use in cosmetics, containing the environmental pollutants, i.e. the fat or oil itself contains free fatty acids. Here, the free fatty acids in the oil or fat acts as the volatile working fluid. Further, free fatty acids in an oil or fat also can contribute to an additive effect in a stripping process by partially acting as an internal working fluid (or by being an active part of the working fluid) in the process. Such oils or fats mentioned above could e.g. be silage oils or oils that have been stored or transported for a long period of time. This means that a volatile working fluid can be added to an oil or fat mixture prior to a stripping process and/or being comprised in the fat or oil mixture containing the environmental pollutants.

In another preferred embodiment of the stripping process, the volatile working fluid is constituted by free fatty acids comprised in a mixture of at least a marine oil, e.g. a fish oil, with a high content of free fatty acids (a low quality marine oil), wherein the free fatty acids in the oil mixture acts as a working fluid. Further, it is hereby possibly to decrease the amount of environmental pollutants and to reduce the amount of free fatty acids in the marine oil at the same time and in the same process.

In another preferred embodiment of the process, the fatty acid esters, fatty acid amides and free fatty acids is obtained from at least one of vegetable, microbial and animal origins. The fatty acid esters mentioned above can e.g. be a by- product from distillation of an ethyl ester mixture prepared by ethylation of a fish oil. In the process industry trade with intermediates is increasing and opens up for an extra financial income.

In another preferred embodiment of the invention the volatile working fluid is of animal origin, preferably a

marine oil e.g. a fish oil or an oil from other marine organism e.g. sea mammals.

In another preferred embodiment of the invention the fat or oil, being edible or for use in cosmetics, is obtained from at least one of vegetable, microbial and/or animal origin. Marine oils that have no or reduced amounts of environmental pollutants are gaining popularity as well as an increasing share of the market. Consequently, removal or reduction of pollutants in e.g. fish oils of high quality as well as fish oils with inferior quality have the potential to substantially increase marketability and value.

It is important to note that the invention is not limited to that the fat or oil, being edible or for use in cosmetics, is used in the process and the volatile working fluid must be of the same origin.

In addition, it is of commercial interest to decrease the amount of pollutants in oil mixtures or blends comprising at least one microbial oil that e.g. will be used in food products or as food supplement (e.g. infant formula) preferable suitable for humans.

In a preferred embodiment of the invention, the stripping process is carried out at temperatures in the interval of 130-270 °C and at a pressure < 1 mbar. Further, if the stripping process is a thin-film evaporation the process is also carried out at mixture flow rates in the range of 10-200 kg/h.m^2.

By using a stripping process, e.g. a distillation method, for decreasing the amount of environmental pollutants in a fat or oil mixture comprising a volatile working fluid it is possible to carry out the stripping processes at lower temperatures, which spare the oil and is at the same time favourable to the end oil product.

Another embodiment of the present invention is a stripping process wherein a working fluid is added to a mixture comprising a fat or an oil, being edible or for use in cosmetics, containing environmental pollutants

prior to a thin-film evaporation process, and the volatile working fluid comprises at least one of fatty acid esters, fatty acid amides, free fatty acids and hydrocarbons (or any combinations thereof).

In a preferred embodiment of the invention, the volatile working fluid is preferable stripped off together with the environmental pollutants by at least one short-path distillation or molecular distillation. This is possible as long as the volatile working fluid is equally or less volatile than the environmental pollutants.

In a preferred embodiment, the volatile working fluid has a volatility that allows it and the environmental pollutants to distill off in a thin-film evaporator, a falling film evaporator, or a short path evaporator at temperatures in the interval of 130°C-270°C.

As mentioned before, by using distillation methods for decreasing the amount of environmental pollutants in a fat or oil mixture in combination with adding a volatile working fluid prior to the mentioned processes it is possible to carry out the stripping processes at lower temperatures, which spares the oil and is at the same time favourable to the end oil product.

In a preferred embodiment of the invention, said stripping process is carried out at a pressure < 1 mbar.

In another preferred embodiment of the invention, the process allows the environmental pollutants to flash off more effective at process conditions of low temperatures and preferable high mixture flow rates. Further, this embodiment offers similar advantages as described above by using the volatile working fluid.

In a preferred embodiment according to the invention the stripping process is carried out by a molecular distillation in the following intervals; mixture flow rates in the interval of 10-200 $kg/h \cdot m^2$, temperatures in the interval of 130-270 °C and a pressure below 1 mbar.

In a more preferred embodiment of the invention the molecular distillation is carried out at temperatures in the interval of 150-220°C and at a pressure below 0,05 mbar.

In a preferred embodiment of the invention, said stripping process is a thin-film evaporation carried out at mixture flow rates in the interval of 10-200 kg/h.m^2.

In a more preferred embodiment of the present invention, said thin-film process is carried out at 10-150 kg/h/m^2 or at flow rates in the range of 400-1200 kg/h at a heated thin film area of 11 m^2; 36-109 kg/h/m^2.

The present invention can also be carried out in one or more subsequent stripping processes.

As mentioned before, the volatile working fluid, being added to an oil or fat mixture prior to at least one thin-film evaporation, is obtained from at least one of vegetable, microbial and/or animal origin, preferably an animal origin, e.g. a marine oil. Further, the fat or oil, being edible or for use in cosmetics, is also obtained from at least one of vegetable, microbial and/or animal origin.

In another preferred embodiment of a process of the present invention, a volatile fat or oil environmental pollutants decreasing working fluid comprises at least one of a fatty acid ester, a fatty acid amide, a free fatty acid and a hydrocarbon and is generated as a fraction product, wherein the fat or oil is edible or for use in cosmetics. This by-product can be used in a new process for decreasing the amount of environmental pollutants in a fat or an oil.

In addition, the volatile working fluid can be a by-product (a distillate fraction) from a regular process for production of ethyl ester concentrates, wherein a mixture comprising an edible or a non-edible fat or oil, preferably a fish oil, is subjected to an ethylating process and preferably a two-step molecular distillation. In the two-step molecular distillation process a mixture

consisting of many fatty acids on ethyl ester form is separated from each other in; a volatile (light fraction), a heavy (residuum fraction) and a product fraction. The volatile fraction from the first distillation is distilled once more and the volatile fraction from the second distillation process is then at least composed of the volatile working fluid, preferably a fatty acid ethyl ester fraction. This fraction consists of at least one of C14 and C16 fatty acids and at least one of the C18 fatty acids from the fat or oil, and is therefore also compatible with the edible or non-edible oil. The fraction can be redistilled one or more times if that is deemed suitable. This prepared working fluid can then be used as a working fluid in a new process for decreasing the amount of environmental pollutants in a fat or oil, wherein the edible or non-edible fats or oils and the oil or fat, being edible or for use in cosmetics, are of the same or different types.

In a preferred embodiment of the invention, the volatile fat or oil environmental pollutants decreasing working fluid is preferably a fatty acid ester (e.g. fatty acid ethyl ester or fatty acid methyl ester), a fatty acid amide or free fatty acids obtained from at least one of vegetable, microbial and animal origins.

In another preferred embodiment of the invention, the volatile fat or oil environmental pollutants decreasing working fluid is obtained from marine oils, e.g. fish or from sea mammals.

In a preferred embodiment of the volatile fat or oil decreasing working fluid, said fat or oil is edible for humans and/or animals or for use in cosmetics.

In another preferred embodiment a health supplement, a pharmaceutical and/or an animal feed product containing oil (end) products, e.g. oil ingredient of fish feed, with a decreased amount of environmental pollutants, prepared according to at least one of the previously mentioned processes is disclosed. For the pharmaceutical and

food supplement industries, it is correct that marine oils be refined in order to increase the content of EPA and/or DHA to suitable levels and the removal or reduction of different kinds of pollutants have the potential to substantially increase marketability and value.

In another embodiment of the invention the pharmaceutical and/or health supplement is preferably intended for treating cardiovascular diseases (CVD) and inflammatory diseases, but they also have positive effects on other CVD risk factors such as plasma lipid profile, hypertension and vascular inflammation.

In another embodiment of the invenion the pharmaceutical and/or health supplement comprises at least one of EPA/DHA ethyl esters and is intented for an range of potential therapeutic applications including; treatment of hypertriglyceridaemia, secondary prevention of myocardial infarction, prevention of atherosclerosis, treatment of hypertension and/or kidney disease and to improve children's learning ability.

Preferably, the pharmaceutical and/or health supplement prepared according to at least one of the previously mentioned processes is based on fish oil.

In addition, there is a demand for marine oils of high quality. This issue forces the fish oil industry to consider alternative refining techniques.

Further, by using one of the processes according to the invention it is now possible to decrease the amount of environmental pollutants and/or to decrease the amount of free fatty acids in e.g. marine oils with inferior quality with a good result. Such oils are appropriate to be used in e.g. animal feed products. If the oil or fat is constituted by high amounts of free fatty acids, said free fatty acids may act as the volatile working fluid in the stripping process.

In another preferred embodiment of the invention the animal feed product is a fish feed product.

In another preferred embodiment of the invention the volatile working fluid comprises at least one of an ester, amides and/or esters composed of longer fatty acids and shorter alcohols or amines, or any combination thereof.

DEFINITIONS

As used herein the term environmental pollutants preferably means pesticides like polychlorinated biphenyls (PCB), DDT and its metabolites, organic compounds found in the sea environment and identified as potentially harmful; Polychlorinated triphenyls (PCTs), dibenzo-dioxins (PCDDs), and dibenzo-furans (PCDFs), Chlorophenols and hexachlorocyclohexanes (HCHs), toxaphenes, dioxins, brominated flame retardants, polyaromatic hydrocarbons (PAH), organic tin-compounds (e.g. tributyltin, triphenyltin) and organic mercury-compounds (e.g. Methyl-Mercury).

As used herein the term oil and fat means fatty acids in at least one of the triglyceride and phospholipid forms. Examples of vegetable oils or fats are corn oil, palm oil, rapeseed oil, soybean oil, sunflower oil and olive oil.

As used herein the term edible means edible for humans and/or animals.

As used herein the term "for use in cosmetics" means an oil or a fat that can be used in products that contributes to enhance humans appearance and/or health, e.g. cosmetic and/or beauty care products.

As used herein the term working fluid is interpreted to include a solvent, a solvent mixture and a fraction, e.g. a fraction from a distillation process, that has a volatility comparable to the volatility of the pollutant/s, preferable equally or less volatile than the pollutant/s, comprising at least one of esters composed of C10-C22 fatty acids and C1-C4 alcohols, amides composed of C10-C22 fatty acids and C1-C4 amines, C10-C22 free fatty acids, mineral oil, hydrocarbons and bio-diesel.

Herein the term equally or less volatile than the pollutants means that the working fluid preferably has an equal or higher boiling point compared to the pollutant/s.

As used herein the term stripping is interpreted to include a general method for removing, separating, forcing or flashing off gaseous compounds from a liquid stream. In addition, the term stripping preferable herein is related to a method/process for decreasing the amount of environmental pollutants in an oil or fat by one or more distilling or distillation processes, e.g. short path distillations, thin-film distillations (thin-film stripping or thin-film (steam) stripping), falling-film distillations and molecular distillations, and evaporation processes. Further, here the term thin-film evaporation also includes falling-film evaporation.

As used herein the term "oils with a low quality" preferably means that the oil contains high amounts of free fatty acids, that makes them less useful for nutritional purposes and that traditional alkaline refining is complicated and costly.

As used herein, the term mineral oil is interpreted to include mineral oil products such as e.g. fractions from distillation processes and white spirit.

As used herein hydrocarbons is interpreted to include organic compounds, that are relatively large molecules composed mainly of carbon and hydrogen. They can also include nuclei of nitrogen, phosphorus, sulphur, and chlorine, among others.

As used herein bio-diesel means a commercial product (or products under development) used as an environment friendly alternative to fuel for cars comprising e.g. methyl esters from preferable vegetable or animal oils.

As used herein the term marine oils includes oil from fish, seal, cetaceans, sea shell and sea mammals. Non limiting examples of fish oils is e.g. Menhaden oil, Cod Liver oil, Herring oil, Capelin oil, Sardine oil, Anchovy oil and Salmon oil. The fish oils mentioned above

may be recovered from fish organs, e.g. cod liver oil, as well as from the meat of the fish.

As used herein the term health supplement is interpreted to include food and food supplement to animals and/or humans, fortification of food, dietary supplement, functional (and medical) food and nutrient supplement.

As used herein the term "treating" means both treatment having a curving or alleviating purpose and treatment having a preventive purpose. The treatment can be made either actutely or chronically.

As used herein the term animal feed product means food or food supplement specially to animals e.g. fish, fowls, pigs and furred (fur-bearing) animal.

As used herein the term fish feed product also includes a fish larvae feed product.

As used herein the term microbial oils also includes "single cell oils" and blends, or mixtures, containing unmodified microbial oils. Microbial oils and single cell oils are those oils naturally produced by micro organisms during their lifespan.

A fat or an oil, being edible or for use in cosmetics, according to the invention can also be a blend of e.g. microbial oils, fish oils, vegetable oils, or any combination thereof.

As used herein the term free fatty acids means fatty acids in free acid form. The free fatty acids is operative as a volatile working fluid and/or included in the fat or oil, being edible or for use in cosmetics.

As used herein the term "together with", means that the volatile working fluid will be stripped off together with, combined with, or adhering the pollutants, namely that the pollutants will accompany the working fluid.

As used herein the term evaporation is an operation used to remove a liquid from a solution, suspension, or emulsion by boiling off some of the liquid. It is thus a thermal separation, or thermal concentration, process. Here the term evaporation process is one that starts with

a liquid mixture and ends with a more concentrated, but still liquid and still concentrate allowing to be pumped as the main product from the process.

As used herein the term acid value of a fat or an oil means the amount of free acids presented in a fat or an oil equal to the number of milligrams of potassium hydroxide needed to neutralize the acid, i.e. that the term serves as an index of the efficiency of refining. This means that a high acid value is characteristic for low quality oil or fat products.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent for one skilled in the art that various change and modifications can be made therein without departing from the spirit and scope thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

The advantages and details of the present invention will become apparent from the following description when taken in conjugation with the accompanying drawings, in which;

FIG 1 is a schematic flow chart of one embodiment illustrating a method for decreasing the amount of environmental pollutants in a fat or an oil, being edible or for use in cosmetics, by adding a volatile working fluid prior to a molecular distillation.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

A number of preferred embodiments of the process for decreasing the amount of environmental pollutants in a mixture comprising a volatile working fluid and a fat or an oil, being edible or for use in cosmetics, containing environmental pollutants will be disclosed below.

A first embodiment of a process for decreasing the amount of environmental pollutants in a fat or an oil, being edible or for use in cosmetics, by adding a volatile working fluid prior to a molecular distillation is

presented in figure 1. The starting fat or oil, being edible or for use in cosmetics, in the first embodiment of the invention is a fish oil whether freshly refined, reverted or mixtures thereof characterized by a level of environmental pollutants. The exact amount of environmental pollutants varies depending upon such factors as fish species, seasonality, geographical catch location and the like.

As used herein the term molecular distillation is a distillation process performed at high vacuum and preferably low temperature (above 130°C). Herein, the condensation and evaporation surface is within the mean molecular path distance, so as to cause the least damage to the oil composition. Further, the cooler is placed in the center of the cylinder comprising heated surface compared to other types of thin-film evaporators where there is a passage to carry out the steam.

The molecular distillation plant illustrated in figure 1, comprises a mixer, a pre-heater, a degasser, a distillation unit and a vacuum pump. In accordance to this embodiment, a volatile working fluid comprising an ethyl ester fraction (of fish oil 6%) is added to a fish oil mixture and blended in a mixer. The oil mixture is then optionally passed through a means for controlling the oil feed rate (herein about 400 kg/h), such as an ordinary throttling valve. The fish oil mixture is then preheated with a heating means such as a plate heat exchanger to provide a preheated fish oil mixture. The mixture is then passed through a degassing step and admitted into the molecular path distance evaporator, a tube including the condensation and evaporation surface. The stripping process is carried out at a pressure between 0,1 and 0,001 mbar and at a temperature of about 200 °C. The fish oil mixture to be concentrated is picked up as it enters the tube by rotating blades. The blades extend nearly to the bottom of the tube and mounted so that there is a clearance of about 1,3 mm between their tips

and the inner surface of the tube. In addition, the blades are driven by an external motor. The fish oil mixture is thrown against the tube wall and is immediately spread into a thin film and is forced quickly down the evaporation surface. The film flows down by gravity and becomes concentrated as it falls. Heated walls and high vacuum strips off the volatile working fluid together with the environmental pollutants, i.e. the more volatile components (distillate) is derived to the closely positioned internal condenser, the less volatile components (residue) continues down the cylinder. The resulting fraction, the stripped fish oil mixture containing at least the fatty acids EPA and DHA is separated and exit through an individual discharge outlet.

In a third embodiment a falling film evaporator is used. In falling film evaporators liquid and vapours flow downwards in parallel flow. The liquid to be concentrated, herein the fish oil mixture, is preheated to boiling temperature. The oil mixture enters the heating tubes via a distribution device in the head of the evaporator, flows downward at boiling temperature, and is partially evaporated. This gravity-induced downward movement is increasingly augmented by the co-current vapour flow. Falling film evaporators can be operated with low temperature differences between the heating media and the boiling liquid, and they also have short product contact times, typically just a few seconds per pass.

In a fourth embodiment of the invention the process is carried out by a short path distillation, which includes the use of a short path evaporator that integrates the features and advantages of thin film or wiped film evaporators but adds internal condensing for applications. Short path evaporators are widely used in fine and specialty chemicals for thermal separation of intermediates, concentration of high value products, and molecular distillation under fine vacuum conditions. Their key features make them uniquely suitable for gentle evaporation

and concentration of heat sensitive products at low pressures and temperatures.

It should be understood that many modifications of the above embodiments of the invention are possible within the scope of the invention such as the latter is defined in the appended claims.

EXAMPLES

The invention will now be illustrated by means of the following non-limiting examples. These examples are set forth merely for illustrative purposes and many other variations of the process may be used. The examples below summarizes some results from different purification of fish oils by molecular distillation.

Equipment and conditions for laboratory experiments

In all the examples below decachlorobiphenyl, 0.60 mg/kg, was added to a fish oil composition as a pollutant model substance. The high chlorine content in decachlorobiphenyl ensures that this compound is less volatile than environmental pollutants like PCB, DDT and its metabolites, toxaphenes, dioxins and brominated flame retardants.

Unless otherwise stated, in all the examples the pressure was 0,001 mbar. However, as this is the lower limit of the pressure indicator, the real pressure will vary from one day to another. That is the reason for somewhat varying results from one example to the next. When the distillation equipment is running under stable conditions, no significant variations are expected. However, this points out that constant pressure is not a very strong condition for carrying out the present invention.

EXAMPLE 1: The effect of adding a working fluid

A fish oil composition containing fatty acids on triglyceride form and decachlorobiphenyl (0,60 mg/kg),

with or without a working fluid, herein an ethyl ester (of fish oil (8%)) was distilled by a laboratory scale molecular distillation at a rate of 600 ml/h and a temperature of 180 °C. The used ethyl ester mixture was a by-product (distillate fraction) from production of EPA and DHA ethyl ester concentrates.

	Decachlorobiphenyl (mg/kg)	Decachlorobiphenyl (% of start value)
Without working fluid	0.43	72
With working fluid	0.022	3.7

The results in the table above show that addition of a volatile working fluid to a fish oil composition has a surprisingly and dramatic effect on the removal of decachlorobiphenyl. Here, more than 95% of the amount of decachlorobiphenyl has been removed ("stripped" off) from the fish oil mixture by molecular distillation.

EXAMPLE 2: The effect of different flow rates.

A fish oil composition containing fatty acids in triglyceride form and decachlorobiphenyl (0,60 mg/kg) was added a working fluid in the form of a ethyl ester fraction in the same way as in example 1. The oil mixture was then stripped by a molecular distillation carried out at different flow rates, but at the same temperature (180 °C).

Flow rate (ml/h)	Decachlorobiphenyl (mg/kg)
400	0.02
600	0.05
1000	0.20

The results given in the table above show that decachlorobiphenyl (and other volatile pollutants) will

be flashed off (reduced) more successfully at lower flow rates. However, the results of optimising the flow rates are less important compared to the effect of adding a working fluid, such as a solvent, solvent mixture or a fraction containing an ethyl ester.

EXAMPLE 3: The effect of different temperatures

Here, an ethyl ester fraction was added to a fish oil composition containing decachlorobiphenyl (0,60 mg/kg) in the same way as in example 1. The oil mixture was then stripped by molecular distillation at different temperatures.

Temperature (°C)	Decachlorobiphenyl (mg/kg)
180	0.11
200	0.04

The table above illustrates that an increased temperature gives an improved removal of pollutants, when a volatile working fluid has been added to the oil mixture prior to a molecular distillation. Further, it is important to know that polyunsaturated fatty acids in fish oil are thermo-labile compounds and an increase in temperature is only applicable within strict limits.

EXAMPLE 4

This example shows an industrial scale process for decreasing the amount of pollutants in a fish oil, which process comprises a step of adding a volatile working fluid to the fish oil mixture prior to a molecular distillation.

63.9 tons of a sardine oil containing different environmental pollutants was added a volatile working fluid in the form of an fatty acid ethyl ester mixture (ethyl ester of fish oil (8%)) before subjecting it to a molecular distillation process. The molecular distillation process was then carried out at a temperature of 200 °C,

a pressure of 0,04 mbar and a mixture flow rate of 300 l/h with a heated surface of 3 m^2.

After treatment, 61.0 tons of purified product were collected. The results in the table below show the content of vitamin A, cholesterol, toxaphenes and dioxins in the sardine oil before and after stripping respectively.

	Before stripping	After stripping
Vitamin A (trans-retinol)	15.3 mg/g	13.0 mg/g
Cholesterol	3.6 mg/g	1.31 mg/g
Toxaphenes	0.3 mg/g	<0.1 mg/g
Dioxins	4.1 pg/g	0.34 pg/g

The results confirm that adding a working fluid to an oil before stripping is effective in reducing the amounts of volatile pollutants at the same time as the concentration of vitamin A, a valuable component in many fish oils, is not seriously affected. This means that this purification method can be used for products that contains vitamin A, e.g. cod liver oil.

In some cases a certain cholesterol level can be of value for some applications of fish oils e.g. for fish feed, especially feed for fish larvae. In these applications it is important to perform a preferential removal only of pollutants.

EXAMPLE 5

A working fluid consisting of ethyl esters of fish oil (8%) was added to an oil produced from farmed salmon. A distillation process was carried out under the same conditions as in example 1 and a distillate fraction of 8.3% was collected. The acid value of the residual oil was reduced from 0.4 before distillation to 0.1 after distillation and the oil was analysed for contaminants before and after processing.

Salmon oil. Content of Indicator-PCBs (μg/kg) before and after processing.

	CB-28	CB-52	CB-101	CB-118	CB-153	CB-105	CB-138	CB-156	CB-180
Before	<3	5	11	<9	16	<3	13	<3	4.8
After	<3	<3	<7	<9	<7	<3	<7	<3	<4

Salmon oil. Content of organochlorine pesticides (μg/kg) before and after processing

	Dieldrin	Endrin	HCB	a-HCH	y-HCH	b-HCH	b-HEPO	pp_DDE	pp_DDD	pp_DDT
Before	22	<3	12	3.8	5.3	<5	<2	38	15	nd*
After	<4	<3	<1	<1	<1	<6	<3	<3	<3	<8

* nd = not detected

The results show that adding a volatile working fluid prior to a stripping (distillation) process is effective in decreasing the amount of preferably organochlorine pesticides in a fish oil composition. In addition, the volatile working fluid also facilitates removal of free fatty acids in the oil. It is hereby possibly to decrease the amount of environmental pollutants and to reduce the amount of free fatty acids in an oil or a fat at the same time and in the same process.

<u>EXAMPLE 6</u>

A fish oil purchased for production of fish feed was destilled by a molecular distillation process under the same conditions as given in example 1 and the start oil had an acid value of 6.8. After removal of a distillate coresponding to 4.3% by weight, the acid value of the residual oil was reduced to 0.2 and the amount of enviromental pollutants in the start oil were decreased in the light fatty acid fraction.

In an identical distillation procedure, an oil with an acid value of 20.5 was destilled. After removal of a distillate of 10.6 % the acid value was reduced to about

1.0 and the amount of environmental pollutants in the start oil were decreased.

Due to the fact that the stripping process in example 5 also facilitates removal of free fatty acids in the oil and that the free fatty acids are volatile it can be expected that even oils with a low quality, i.e. a high content of free fatty acids, can be treated successfully according to the invention. An example of oils with low quality is fish oils used for production of fish feed, silage oils or oils that have been stored or transported for a long period of time.

This example therefore shows that a stripping process for decreasing the amount of environmental pollutants in a mixture comprising at least a fat or an oil with a high content of free fatty acids (a low quality oil or fat) is effective since the free fatty acids in the oil or fat acts as a working fluid. Further, the free fatty acids in the oil or fat also contributes to an additive effect in the stripping process by partially acting as an internal working fluid (or by being an active part of the working fluid) in the stripping process.

A person known in the art will also realise that the same stripping effect can be obtained by adding a volatile working fluid containing a similar volume of suitable free fatty acids to an oil or fat containing environmental pollutants in order to decrease the amount ofenvironmental pollutants in the fat or oil.

CLAIM

1. A process for decreasing the amount of environmental pollutants in a mixture comprising a volatile working fluid and a fat or an oil, being edible or for use in cosmetics, containing the environmental pollutants, which process comprises stripping from the mixture the volatile working fluid and the environmental pollutants, c h a r a c t e r i z e d in that the volatile working fluid comprises at least one of a fatty acid ester, a fatty acid amide, a free fatty acid and a hydrocarbon.

2. A process according to claim 1, wherein the volatile working fluid is constituted by free fatty acids comprised in the fat or oil, being edible or for use in cosmetics, containing the environmental pollutants.

3. A process according to claim 1, wherein the at least one of a fatty acid ester, a fatty acid amide and a free fatty acid is obtained from at least one of vegetable, microbial and animal origins.

4. A process according to claim 3, wherein the animal origin is fish or sea mammals.

5. A process according to claim 1, wherein said stripping process is carried out at temperatures in the interval of 130-270 °C.

6. A process according to claim 1, wherein said stripping process is carried out at a pressure below 1 mbar.

7. A process according to claim 1, wherein the fat or oil, being edible or for use in cosmetics, is obtained from at least one of vegetable, microbial and animal origins.

8. A process for decreasing the amount of environmental pollutants in a mixture comprising a volatile working fluid and a fat or an oil, being edible or for use in cosmetics, containing the environmental pollutants, which process comprises at least one of thin-film evaporation c h a r a c t e r i z e d in employing a step of adding a volatile working fluid to the mixture prior to at least one of thin-film evaporation, and the volatile working fluid comprises at least one of a fatty acid ester, a fatty acid amide, a free fatty acid and a hydrocarbon.

9. A process according to claim 8, wherein the at least one thin-film evaporation is a molecular distillation.

10. A process according to claim 8, wherein the at least one thin-film evaporation is a short-path distillation.

11. A process according to claim 8, wherein the at least one of a fatty acid ester, a fatty acid amide and a free fatty acid is obtained from at least one of vegetable, microbial and animal origins.

12. A process according to claim 11, wherein the animal origin is fish or sea mammals.

13. A process according to claim 8, wherein at least one thin-film evaporation process is carried out at mixture flow rates in the interval of 10-200 $kg/h \cdot m^2$.

14. A process according to claim 8, wherein at least one thin-film evaporation process is carried out at temperatures in the interval of 130-270 °C.

15. A process according to claim 8, wherein the at least one thin-film evaporation process is carried out at pressure below 1 mbar.

16. A process according to claim 8, wherein the fat or oil, being edible or for use in cosmetics, is obtained from at least one of vegetable, microbial and animal origins.

17. A volatile fat or oil environmental pollutants decreasing working fluid, comprising at least one of a fatty acid ester, a fatty acid amide, a free fatty acid and a hydrocarbon.

18. A volatile fat or oil environmental pollutants decreasing working fluid according to claim 17, wherein at least one of a fatty acid ester, a fatty acid amide, a free fatty acid is obtained from at least one of vegetable, microbial and animal origins.

19. A volatile fat or oil environmental pollutants decreasing working fluid according to claim 17, wherein the animal origin is fish or sea mammals.

20. A volatile fat or oil environmental pollutants decreasing working fluid according to claim 17, wherein the fat or oil is edible or for use in cosmetics.

21. A health supplement prepared according to at least one of the processes presented in claims 1 and 8.

22. A pharmaceutical based on fish oil prepared according to at least one of the processes presented in claims 1 and 8.

23. An animal feed product prepared according to at least one of the processes presented in claims 1 and 8.

24. An animal feed product according to claim 23, wherein the feed product is a fish feed product.

SUMMARY OF THE INVENTION

The invention relates to a process for decreasing the amount of environmental pollutants in a mixture comprising a volatile working fluid and a fat or an oil, being edible or for use in cosmetics, containing the environmental pollutants, which process comprises stripping from the mixture the volatile working fluid and the environmental pollutants. The present invention also relates to a second process with the same purpose as presented above, which process comprises thin-film evaporation. In addition, the present invention relates to a volatile fat or oil environmental pollutants decreasing working fluid, a health supplement, a pharmaceutical and an animal feed product prepared according to at least one of the processes mentioned above.

Figure 1

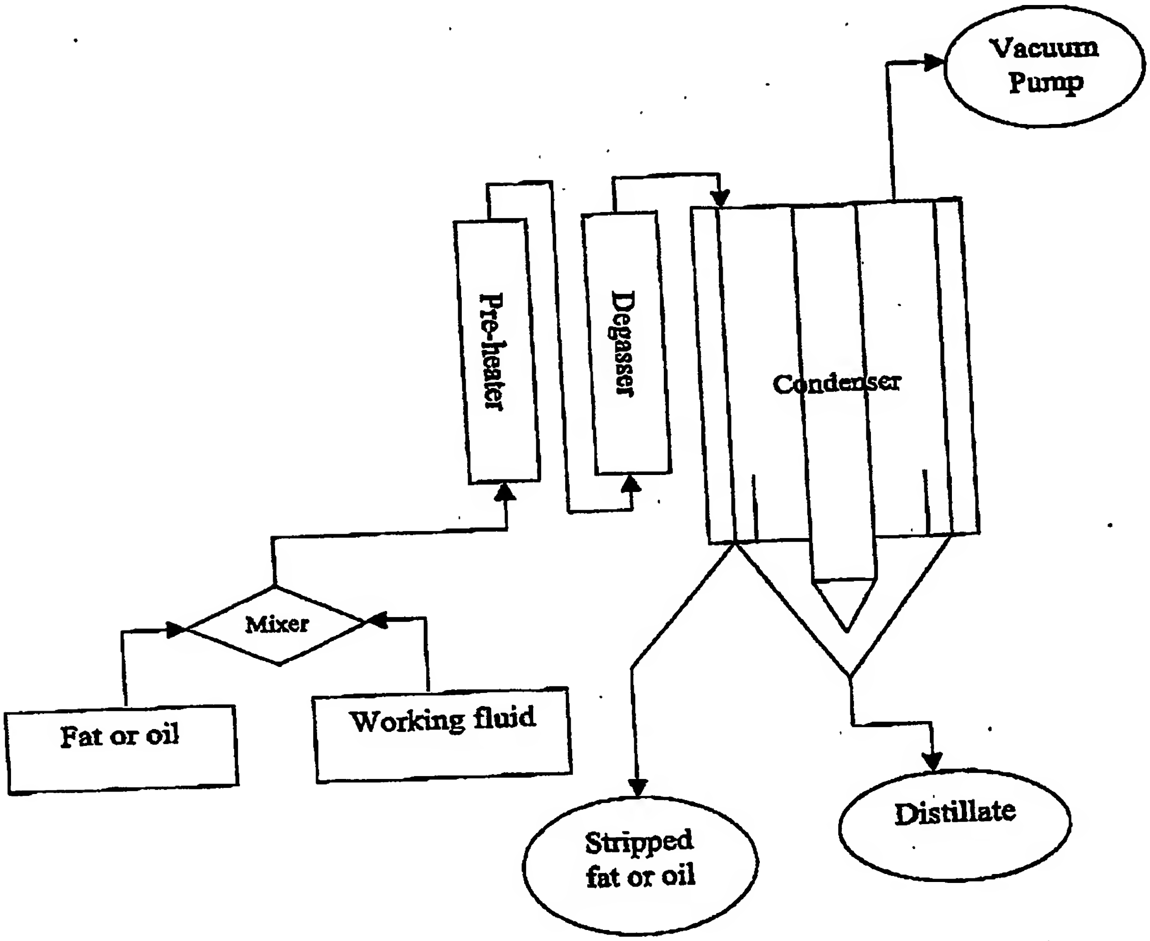
Vacuum Pump
Pre-heater
Degasser
Condenser
Mixer
Fat or oil
Working fluid
Stripped fat or oil
Distillate

Figure 1/1